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Spectrum and term system of trebly ionized silicon, Si IV

By YNGVE G. TORESSON

With 1 plate and 4 figures in the text

SUMMARY

The spectrum of trebly ionized silicon has been studied in the region 10000–400 Å by using a sliding spark in vacuum. A total of 58 spectrum lines above 2000 Å have been measured and classified, 34 of which had not been observed before. In the vacuum ultraviolet region some previously known multiplets have been accurately measured. New levels have been added to those previously known, and the whole term system has been recalculated on the basis of the new measurements. The narrow splittings of the terms $3d$, $4d$ and $5d\,^2D$ have been determined.

Introduction

The spark spectra of silicon have been the subject of several investigations. Before Fowler's work they had been studied by Millikan and Bowen (1924, 1925), McLennan and Shaver (1924), Barrell (1923), Sawyer and Paton (1923), and others. Fowler published in 1925 a comprehensive study of the spectra of silicon, including Si IV, through the region 6700 Å–1400 Å. Bowen (1928, 1932) then added a doublet of Si II and some lines of Si III in the vacuum region. In 1933 Edlén and Söderqvist recalculated and extended the term system of Si IV on the basis of new measurements in the region 4328 Å–815 Å. Jackson (1934) has made some interferometric wavelength determinations for certain silicon lines occurring in B- and O-type stars. Some additional data for Si II have been published by Kiess (1938) in connection with his study of Si I.

The present investigation was started for the purpose of extending the spectroscopic laboratory data on the spark spectra of silicon, especially in the red and infrared regions, which have recently become of increased interest through the use of infrared-sensitive plates in the study of stellar spectra.

Fowler used capillary tubes of 1 mm internal diameter or less, filled with silicon tetrafluoride and excited by induction-coil discharges of varying intensity, whereas Edlén and Söderqvist used a condensed spark in vacuum between poles of fused silicon. Jackson's light source was a condensed discharge through silicon tetrafluoride at a pressure of 0.005–0.05 mm Hg.

Since Bockasten (1955, 1956) had successfully used a sliding vacuum-spark in his investigation of C III and C IV and had found that this light source shows much less Stark effect than the conventional vacuum spark, it was natural to try a sliding vacuum-spark in the present investigation. The spark described below was found to

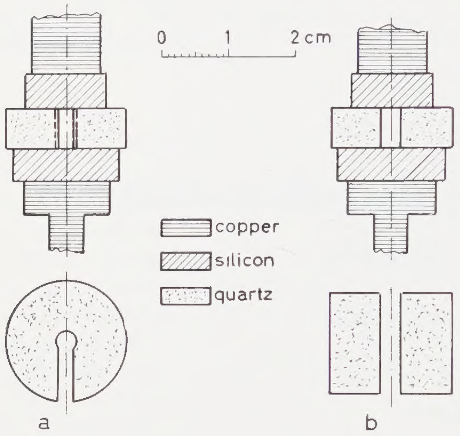

Fig. 1. Electrode arrangement for the sliding spark. In Fig. 1b the insulating disk is cut into two parts in order to avoid a continuous background due to thermal radiation.

produce not only the spectra of Si II and Si III but also a very complete spectrum of Si IV. By regulating the conditions which determine the current density it was possible to separate the different ionization stages and to considerably reduce the Stark effect.

The light source

The vacuum-spark chamber described by Bockasten (1955) was used, with some modifications, in the present investigation. As silicon is a poor conductor at ordinary temperatures, the electrodes have to be short and their temperature must be near the melting-point of silicon. At this temperature silicon is a good electrical conductor, and the spark readily passed through the slit in the quartz disk (see Fig. 1). At a somewhat higher temperature the electrodes melted and molten silicon filled the slit so that the light could not reach the spectrograph. If, on the other hand, the temperature was too low, the spark did not pass in the slit but on the outside of the disk. The usable temperature range was rather narrow. The number of sparks per second was adjusted so as to give the right electrode temperature. If silicon is mixed with a trace of another metal, for instance boron or aluminium, the conductivity is improved, but since the added metal would complicate the spectrum, pure silicon was preferred in this investigation.

The silicon electrodes were supplied by "Institutet för Halvledarforskning", Stockholm. The size of the electrodes proved to be rather critical. If the silicon plates have a diameter of 5–8 mm and a thickness of 2–3 mm, the spark works well, but the silicon melts quickly, and the quartz disk must be cleaned very often. Plates having the dimensions shown in Fig. 1 proved to be more suitable. If the diameter is made larger and a thickness of 3 mm is retained, the silicon does not melt so quickly, but the plates are more liable to break when the light source is cleaned. By using a thickness of 5 mm and a diameter of 12 mm for the upper silicon plate and 16 mm for the lower one, a frequency of up to 20 sparks per second can be maintained, and it is possible to use the plates for several times.

In order to cool the vacuum-spark chamber, four pipes were inserted through the brass walls of the cube and connected by rubber tubes through which water circulated.

The upper, insulated electrode was cooled by a fan. The pressure in the vacuum chamber was measured with a thermocouple gauge. The light source worked well at a pressure of 10^{-3} mm Hg or less. The power supply and the spark circuit were the same as used by Bockasten (1955). Lines of different stages of ionization were separated by varying the length of the external spark gap and the number of turns of the inductance coil, as described by Bockasten.

For the study of Si III and Si IV an external spark gap of 2–6 mm and an inductance of 20–29 turns of the coil were used. Only a few faint lines of Si IV required a spark gap of 8 mm and 15 turns of the coil. Spark gaps of 2, 4, 6, and 8 mm corresponded to voltages of 8, 13, 16, and 19 kV, respectively. The circuit contained a capacitance of 0.30 μF. A frequency of ten to twenty sparks per second was used. After running the spark for about an hour at this frequency it was necessary to clean the quartz disk and reshape the electrodes.

Spectrograms

The spectrum from 10000 Å to 2000 Å was photographed with a stigmatic, concave-grating spectrograph (Jarrell-Ash) having a plate factor of about 5 Å/mm in the first order. The region 4700 Å–3000 Å was measured preferably in the second order and most lines from 3000 Å to 2300 Å in the third order. Some lines between 2300 Å and 2100 Å were measured in the fourth order. Some measurements of strong lines in the region 5300 Å–4300 Å have also been made on spectrograms taken with a prism spectrograph described by Minnhagen (1944). The plate factor for this spectrograph is between 3.2 and 1.3 Å/mm for the range used.

Eastman Kodak spectroscopic plates of different types were used throughout. Overlapping orders could be separated in most cases by using a suitable combination of emulsion type and Jena glass filters. For those spectrograms that have been measured the exposure times ranged from 2 min to 90 min in the first and second orders, and from 3 min to 15 min in the third and fourth orders.

To separate different stages of ionization three exposures with different amounts of inductance and different lengths of the outer spark gap were taken for each region of the spectrum. With a spark gap of 2 mm and 29 turns of the induction coil the current density was reduced to the limit where most of the Si IV lines began to disappear. Only sixteen of the strongest lines of the Si IV spectrum above 2000 Å were measured under these conditions. The other lines were measured on plates taken with such current densities that they just appear, which usually corresponds to a spark gap of 4 mm and 20 turns of the coil. In this way the influence of Stark effect has been reduced as far as possible.

SiO bands appeared in the region 4300 Å–2200 Å, but these bands were troublesome in the measurement of only a few faint lines in the spectrum of Si IV. A strong spectrum of O II, probably from the quartz disk, is present on all spectrograms. Cu I, Cu II, and some Zn I came from the electrode holders. These lines were easily identified and could be used as reference lines. From 2500 Å to 2000 Å the Cu II wave-lengths listed by Shenstone (1955) have been used, and in the region 4700 Å–4300 Å the O II wave-lengths given by Beals (1931) provided additional references.

The spectrograms were furnished with iron reference spectra by means of an iron arc in air, which was adjusted so that the light passed through the same quartz-fluorite lens as the light from the vacuum spark, and was imaged in the plane of the spectrograph slit exactly where the spark was imaged. No shift between lines from the spark and lines from the iron arc could be found on the spectrograms taken with the Jarrell-Ash spectrograph. On spectrograms taken with the prism spectrograph, however, such a shift, ranging from 0.010 Å to 0.090 Å, was found and was corrected for. The iron spectra were usually of the same diffraction order as the silicon spectra. First-order silicon lines in the region 10000 Å–7200 Å, however, were measured against second-order iron lines, and the measurements of silicon spectra in the third and fourth orders were made against second- and third-order iron lines. For the long-wave region Ne I and Ar I reference spectra were obtained by means of Geissler tubes. The internationally adopted standards of iron, neon, and argon provided a sufficient number of reference lines from 10000 Å to 2400 Å.

The spectrograms of the vacuum ultraviolet region will be described in a forthcoming paper on Si III.

Si IV lines in the region 10000 Å–2000 Å

All Si IV lines observed and measured in this region by means of the sliding vacuum spark are given in Table 1. The table contains a total of 58 measured lines from 9018 Å to 2120 Å, of which 22 are in the region above 4654 Å, where no line had been observed before. Some additional lines from higher terms could be observed, but they were too hazy to be measured.

The estimated intensities are given on a logarithmic scale. They refer to spectrograms exposed for the same length of time, under the same spark conditions, and on the type of plate that is most sensitive in each region.

The wave-lengths are weighted means of measurements on two to eight spectrograms, except in the case of a few faint lines that were measured on one spectrogram only. The estimated uncertainty is about 0.02 Å or less for the values that are given with three decimals. In most other cases the error is believed not to exceed 0.04 Å. The wave-numbers in the fourth column of Table 1 were derived from the wave-lengths in column 2 by using Edlén's (1953) table of vacuum corrections. The wave-numbers given for λ 4116 and λ 4088 correspond to Jackson's wave-lengths.

The differences between the new measurements and Fowler's are generally small and not of a systematic character. If $\lambda\lambda$ 4654 and 4631 are excluded, the differences vary from -0.04 Å to $+0.03$ Å, and the mean difference is 0.00 Å. The transitions $5g\,^2G$–$6h\,^2H$ (λ 4654) and $5f\,^2F$–$6g\,^2G$ (λ 4631) are exceptional in that they show a shift of $+0.18$ Å and -0.14 Å, respectively, which must be attributed to the Stark effect in Fowler's light source. Stark effect would also be expected to influence the transition $5g\,^2G$–$7h\,^2H$ at 2904 Å observed by Edlén and Söderqvist. This transition is blended by a strong line of Si II, but in the third order the lines are well separated. The transition $5p\,^2P$–$6d\,^2D$ is very faint, and the identification of this doublet by Edlén and Söderqvist is probably not correct.

It is remarkable that Fowler could resolve the doublet $4f\,^2F$–$5g\,^2G$ but not the doublet $4f\,^2F$–$5d\,^2D$. In the present investigation $4f\,^2F$–$5d\,^2D$ shows a measurable splitting in the third order (see Fig. 3), whereas $4f\,^2F$–$5g\,^2G$ shows no sign of separation even in that order. This finding is in accord with the predicted structure. While the splitting of $5g\,^2G$ may be assumed to be close to the hydrogenic value, $+0.60$ cm^{-1}, the observations indicate a splitting for $5d\,^2D$ of only $+0.10$ cm^{-1}. Consequently, the difference between the main components should be larger for $4f\,^2F$–$5d\,^2D$ than for $4f\,^2F$–$5g\,^2G$. Also, the higher sensitivity of $5g\,^2G$ to Stark-effect broadening should contribute to make the former doublet easier to separate than the latter.

Table 1. Si IV lines in the region 10 000–2 000 Å

Description of lines:

bl = blended by
h = hazy
H = very hazy
l = shaded to longer waves
m = masked by
s = shaded to shorter waves

References to previous measurements:

ES = Edlén and Söderqvist (1933), F = Fowler (1925), J = Jackson (1934).

Intensity and shape	λ_{air}, Å	Previous measurements	Wave-number, cm^{-1}		Combination
			obs.	calc.[1]	
1 *h*	9018.162		11 085.69	5.72	$5s\,^2S_1-5p\,^2P_1$
2 *h*	8957.245		11 161.08	1.08	$^2S_1-\ ^2P_2$
1 *h*	8240.606		12 131.70	1.70	$6f\,^2F-7d\,^2D$
1 *h*	7752.905		12 894.84	4.76	$6g\,^2G-7f\,^2F$
1 *h*	7730.469		12 932.27	2.28	$6h\,^2H-7g\,^2G$
2 *H*	7725.64		12 940.3	39.76	$6h\,^2H-7h\,^2H$
6 *h s*	7723.818		12 943.40	^2I	$6h\,^2H-7i\,^2I$
5 *h l*	7718.785		12 951.84	1.84	$6g\,^2G-7h\,^2H$
4 *h l*	7678.748		13 019.37	9.37	$6f\,^2F-7g\,^2G$
4 *h*	7654.555		13 060.52	0.52	$6p\,^2P_2-7s\,^2S_1$
2 *h*	7630.497		13 101.70	1.69	$^2P_1-\ ^2S_1$
4 *h*	7068.410		14 143.55	3.60	$5d\,^2D_2-6p\,^2P_1$
6 *h*	7047.939		14 184.63	4.67 4.77	$^2D_3-\ ^2P_2$ $^2D_2-\ ^2P_2$
3 *h*	6998.358		14 285.13	5.12	$6d\,^2D-7f\,^2F$
7	6701.207		14 918.57	8.47 8.57	$5p\,^2P_2-5d\,^2D_2$ $^2P_2-\ ^2D_3$
5	6667.556		14 993.86	3.83	$^2P_1-\ ^2D_2$
1 *h*	5309.493		18 828.95	^2P	$6d\,^2D_2-8p\,^2P_1$
2 *h*	5304.971		18 845.00	^2P	$^2D_{2,3}-\ ^2P_2$
3	4950.105		20 195.95	5.93	$5f\,^2F-6d\,^2D$
2 *h*	4673.297		21 392.18	2.35	$5g\,^2G-6f\,^2F$
1 *H*	4667.14		21 420.4	0.42	$6f\,^2F-8g\,^2G$
3 *H*	4656.92		21 467.4	7.36	$5g\,^2G-6g\,^2G$
10 *h s*	4654.323	4.14 F	21 479.39	9.44	$5g\,^2G-6h\,^2H$
1 *h l*	4647.45		21 511.1	1.28	$5f\,^2F-6f\,^2F$
9 *h l*	4631.241	1.38 F	21 586.44	6.29	$5f\,^2F-6g\,^2G$
3 *H*	4628.62		21 598.6	8.37	$5f\,^2F-6h\,^2H$
0 *h*	4611.27		21 679.9	9.70	$6p\,^2P_2-7d\,^2D_{3,2}$
m 0 II	(4602.578)		21 720.	0.87	$^2P_1-\ ^2D_2$
m 0 II	(4416.506)		22 635.	5.98	$6s\,^2S_1-7p\,^2P_1$
0 *h*	4411.652		22 660.88	^2P	$^2S_1-\ ^2P_2$
2 *h l*	4403.734		22 701.63	^2F	$6d\,^2D-8f\,^2F$
5	4328.175	8.22 ES	23 097.93	7.92	$5p\,^2P_2-6s\,^2S_1$
3	4314.104	4.18 ES	23 173.27	3.28	$^2P_1-\ ^2S_1$
7 *h l*	4212.407	2.44 F	23 732.71	2.71	$5d\,^2D-6f\,^2F$
9	4116.097	6.104 F; 6.103 J	24 287.97 J	7.97	$4s\,^2S_1-4p\,^2P_1$
10	4088.854	8.863 F; 8.862 J	24 449.78 J	9.78	$^2S_1-\ ^2P_2$
2 *h*	4038.057		24 757.39	^2S	$6p\,^2P_2-8s\,^2S_1$
1 *h bl* band	4031.39		24 798.3	8.56	$^2P_1-\ ^2S_1$
6	3773.151	3.13 F	26 495.52	5.53	$4d\,^2D_2-5p\,^2P_1$

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[1] A letter in this column indicates that the high term is determined from this line alone.

Table 1 (cont.)

Intensity and shape	λ_{air}, Å	Previous measurements	Wave-number, cm^{-1}		Combination
			obs.	calc.[1]	
8	3762.435	2.41 F	26 570.98	0.89 1.01	$4d\ ^2D_2 - 5p\ ^2P_2$ $^2D_3 - \ ^2P_2$
1 *h*	3244.192		30 815.43	^2P	$5d\ ^2D_2 - 7p\ ^2P_1$
m Si III	(3241.583)		30 840.	0.23	$^2D_3 - \ ^2P_2$
m Si III	(3241.572)		30 840.	0.33	$^2D_2 - \ ^2P_2$
9	3165.710	5.72 F	31 579.35	9.35 9.47	$4p\ ^2P_2 - 4d\ ^2D_3$ $^2P_2 - \ ^2D_2$
7	3149.561	9.56 F	31 741.27	1.28	$^2P_1 - \ ^2D_2$
1 *h*	2971.522		33 642.96	2.98	$5f\ ^2F - 7d\ ^2D$
2 *h*	2904.470	4.3 ES	34 419.60	9.20	$5g\ ^2G - 7h\ ^2H$
3 *h l*	2895.131	5.13 F	34 530.63	0.65	$5f\ ^2F - 7g\ ^2G$
3 *h*	2723.812	3.81 F	36 702.38	2.48	$5d\ ^2D - 7f\ ^2F$
1 *bl* band	2677.57	7.19 ES	37 336.1	5.89	$5p\ ^2P_2 - 6d\ ^2D_{3,2}$
4	2675.249	5.26 F	37 368.59	8.57	$4f\ ^2F_4 - 5d\ ^2D_3$
4	2675.120		37 370.39	0.42 0.52	$^2F_3 - \ ^2D_2$ $^2F_3 - \ ^2D_3$
1	2672.193	1.88 ES	37 411.33	1.25	$5p\ ^2P_1 - 6d\ ^2D_2$
7	2517.506	7.56 F 7.48 F	39 709.90	9.73[2]	$4f\ ^2F_4 - 5g\ ^2G_{5,4}$ $^2F_3 - \ ^2G_4$
1	2485.378		40 223.19	3.15	$5s\ ^2S_1 - 6p\ ^2P_1$
2	2482.816	2.66 ES	40 264.68	4.32	$^2S_1 - \ ^2P_2$
3	2370.985	1.04 F	42 163.69	3.76	$5p\ ^2P_2 - 7s\ ^2S_1$
2	2366.755		42 239.04	9.12	$^2P_1 - \ ^2S_1$
2 *H*	2328.56		42 931.9	1.70	$5f\ ^2F - 8g\ ^2G$
5 *h*	2287.041	7.08 F	43 711.13	0.92	$4d\ ^2D - 5f\ ^2F$
4	2127.467	7.48 F	46 989.41	9.28	$4p\ ^2P_2 - 5s\ ^2S_1$
3	2120.179	0.19 F	47 150.91	1.09	$^2P_1 - \ ^2S_1$

[1] A letter in this column indicates that the high term is determined from this line alone.

[2] The centre of gravity is calculated.

The term system

The simple one-electron system of Si IV is illustrated by the term diagram shown in Fig. 2. The term values were calculated from the carefully weighted wave-numbers of Table 1 by using the method of least squares. Bockasten (1955) has given a convenient procedure for this calculation. The centres of gravity were used for the terms $4d\ ^2D$, $5d\ ^2D$, and $4f\ ^2F$ in the calculation. The deep terms $3s\ ^2S$, $3p\ ^2P$, and $3d\ ^2D$ have been connected with the upper part of the term system by the aid of four vacuum-ultraviolet multiplets. The wave-lengths, given in the fourth column of Table 2, are weighted means of measurements on several spectrograms relative to lines of C I, N I, N II, O I, O II, Mg II, Ar II, Ca II, and Cu II.

The relative term values thus obtained are given in Table 3 under the heading *E*. New terms are $8s\ ^2S$, $7p$, $8p\ ^2P$, $6d$, $7d$, $8d\ ^2D$, $8f\ ^2F$, $8g\ ^2G$, and $7i\ ^2I$, of which $8d\ ^2D$ is predicted. The agreement between observed and recalculated wave-numbers indicates an average accuracy of about $\pm 0.1\ cm^{-1}$ in the tabulated level-values. A comparison with the term values in Atomic Energy Levels, which are based on the

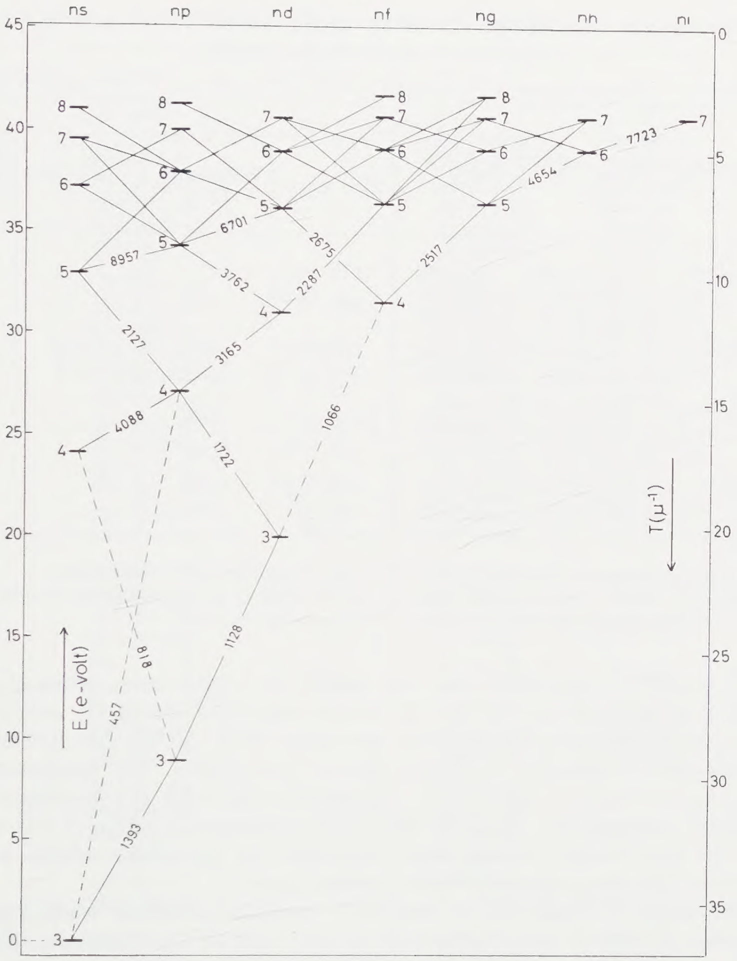

Fig. 2. Term diagram for Si IV. Solid lines indicate the observed transitions that were used for the calculation of the term system. The transition $3p$–$4s$, though shown by a dotted line, was also included in the calculation.

paper by Edlén and Söderqvist, reveals differences ranging from -5.3 cm^{-1} to -1.2 cm^{-1}. The main part of these differences originates in the vacuum-ultraviolet wave-lengths.

It has not been possible to resolve any of the $nd\,^2D$ terms directly, but the splittings are revealed by the differences between the observed intervals of their combinations with ^2P terms and the true ^2P intervals. When calculating the ^2D intervals it was assumed that the observed position of the unresolved blend of $^2P_2$–$^2D_3$ and $^2P_2$–$^2D_2$ corresponds to the centre of gravity of the two components, weighted in the ratio 9:1. The splitting of $3d\,^2D$ turns out to be -1.19 cm^{-1}, and that of $4d\,^2D$, -0.12 cm^{-1}. For $5d\,^2D$ one finds $+0.10$ cm^{-1}, and it may be assumed that the higher ^2D terms will all have a positive splitting. Actually, the observations indicate a positive

Table 2. Multiplets connecting the deep terms, $3s\,^2S$, $3p\,^2P$, and $3d\,^2D$, with the upper part of the term system.

Combination	$\sigma_{\text{calc.}}$, cm^{-1}	$\lambda_{\text{calc.}}$, Å	$\lambda_{\text{obs.}}$, Å			
			This work	Shenstone[1] 1958	Edlén[2]	Edlén and Söderqvist 1933
$3d\,^2D_2–4p\,^2P_1$	57 891.26	1727.376	.377 (5)	.417		.38
$^2D_2–\ ^2P_2$	58 053.07	1722.562	.534 (6)	.575		.52
$^2D_3–\ ^2P_2$	58 054.26	1722.526				
$3s\,^2S_1–3p\,^2P_1$	71 287.54	1402.770	.769 (12)	.766	.766	.73
$^2S_1–\ ^2P_2$	71 748.64	1393.755	.755 (15)	.758	.750	.73
$3p\,^2P_2–3d\,^2D_3$	88 625.77	1128.340	.340 (10)	.358		.326
$^2P_2–\ ^2D_2$	88 626.96	1128.325				
$^2P_1–\ ^2D_2$	89 088.06	1122.485	.486 (8)	.506		.495
$3p\,^2P_2–4s\,^2S_1$	122 230.25	818.128	.129 (8)	.132		.121
$^2P_1–\ ^2S_1$	122 691.35	815.053	.049 (7)	.059		.060

[1] Unpublished measurements kindly furnished by Professor A. G. Shenstone.

[2] Unpublished values measured on spectra taken with a 2-metre normal-incidence vacuum spectrograph at the Massachusetts Institute of Technology in 1937.

separation for $6d\,^2D$ and $7d\,^2D$, but the values are of the same order of magnitude as the observational errors. Of the ^2F levels only $4f\,^2F$ could be resolved. Fig. 3 shows a microphotometer record of the transition $4f\,^2F–5d\,^2D$. The spectrogram was taken in the third order with a plate factor of 1.58 Å/mm. The measurements give a splitting in $4f\,^2F$ of 1.9 cm^{-1}, which agrees exactly with the separation deduced from Fowler's observation of $4f\,^2F–5g\,^2G$. The hydrogenic value of the splitting of $4f\,^2F$ is 1.95 cm^{-1}, which, being thus confirmed by the observations within their limits of error, has been adopted in the present work.

From the levels in Table 3 one can now calculate accurate wave-lengths for a great number of lines in the vacuum-ultraviolet part of the spectrum. Since silicon

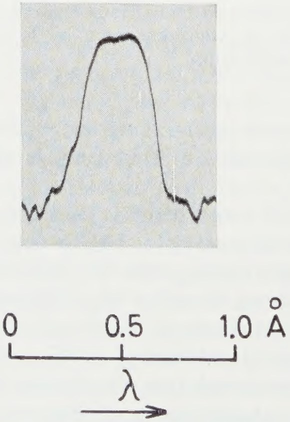

Fig. 3. Microphotometer record of the transition $4f\,^2F–5d\,^2D$.

Table 3. Term values of Si IV.

Term symbol	E, cm^{-1}	ΔE, cm^{-1}	T, cm^{-1}	n^*	Δn^*
$3s\ ^2S_1$	0.00		364 093.05	2.195 971 6	
$4s\ ^2S_1$	193 978.89		170 114.16	3.212 644 6	
$5s\ ^2S_1$	265 417.95		98 675.10	4.218 219 0	
$6s\ ^2S_1$	299 676.95		64 416.10	5.220 784	
$7s\ ^2S_1$	318 742.79		45 350.26	6.222 186	
$8s\ ^2S_1$	330 439.66		33 653.39	7.223 015	
$3p\ ^2P_1$	71 287.54	+ 461.10	292 805.51	2.448 743 5	0.001 930 3
$^2P_2$	71 748.64		292 344.41	2.450 673 8	
$4p\ ^2P_1$	218 266.86	+ 161.81	145 826.19	3.469 885 5	0.001 926 7
$^2P_2$	218 428.67		145 664.38	3.471 812 2	
$5p\ ^2P_1$	276 503.67	+ 75.36	87 589.38	4.477 207	0.001 927
$^2P_2$	276 579.03		87 514.02	4.479 134	
$6p\ ^2P_1$	305 641.10	+ 41.17	58 451.95	5.480 667	0.001 931
$^2P_2$	305 682.27		58 410.78	5.482 598	
$7p\ ^2P_1$	322 312.93	+ 24.90	41 780.12	6.482 583	0.001 932
$^2P_2$	322 337.83		41 755.22	6.484 515	
$8p\ ^2P_1$	332 743.87	+ 16.05	31 349.18	7.483 759	0.001 917
$^2P_2$	332 759.92		31 333.13	7.485 676	
$3d\ ^2D_2$	160 375.60	− 1.19	203 717.45	2.935 743 0[1]	
$^2D_3$	160 374.41		203 718.64		
$4d\ ^2D_2$	250 008.14	− 0.12	114 084.91	3.923 003 3[1]	
$^2D_3$	250 008.02		114 085.03		
$5d\ ^2D_2$	291 497.50	+ 0.10	72 595.55	4.917 882 [1]	
$^2D_3$	291 497.60		72 595.45		
$6d\ ^2D$	313 914.92		50 178.13	5.915 285	
$7d\ ^2D$	327 361.97		36 731.08	6.913 788	
$8d\ ^2D$	336 051.55		28 041.50	7.912 838 [2]	
$4f\ ^2F_3$	254 127.08	+ 1.95	109 965.97	3.995 820 3[1]	
$^2F_4$	254 129.03		109 964.02		
$5f\ ^2F$	293 718.99		70 374.06	4.994 898	
$6f\ ^2F$	315 230.27		48 862.78	5.994 374	
$7f\ ^2F$	328 200.04		35 893.01	6.994 038	
$8f\ ^2F$	336 616.55		27 476.50	7.993 780	
$5g\ ^2G$	293 837.92		70 255.13	4.999 124	
$6g\ ^2G$	315 305.28		48 787.77	5.998 980	
$7g\ ^2G$	328 249.64		35 843.41	6.998 875	
$8g\ ^2G$	336 650.69		27 442.36	7.998 751	
$6h\ ^2H$	315 317.36		48 775.69	5.999 723	
$7h\ ^2H$	328 257.12		35 835.93	6.999 606	
$7i\ ^2I$	328 260.76		35 832.29	6.999 961	

[1] n^* given for centre of gravity.
[2] Extrapolated value.

commonly occurs as an impurity in vacuum-ultraviolet spectra, it may be useful to have a finding list for Si IV in this region. Such a list of calculated Si IV lines is given in Table 4. The starred values, which depend exclusively on observations above 2000 Å, should be reliable to about 0.004 Å at 1800 Å and to 0.001 Å at 900 Å. The errors in the other wave-lengths are estimated to range from 0.004 Å at 1100 Å to 0.0004 Å at 300 Å.

Table 4. The vacuum-ultraviolet spectrum of Si IV.

Calculated wavelengths of all transitions involving quantum numbers up to $n = 6$. Starred values are based entirely on observations above 2 000 Å.

Combination	λ_{calc}, Å	λ_{obs}, Å
$4d\ {}^2D_2{-}6p\ {}^2P_1$	1797.496*	
${}^2D_2{-}\quad {}^2P_2$	1796.166*	
${}^2D_3{-}\quad {}^2P_2$	1796.162*	
$3d\ {}^2D_2{-}4p\ {}^2P_1$	1727.376	.377 (5)
${}^2D_2{-}\quad {}^2P_2$	1722.562	.534 (6)
${}^2D_3{-}\quad {}^2P_2$	1722.526	
$4f\ {}^2F\ {-}6d\ {}^2D$	1672.612*	
$4f\ {}^2F\ {-}6g\ {}^2G$	1634.599*	.607 (1)
$4d\ {}^2D\ {-}6f\ {}^2F$	1533.220*	
$3s\ {}^2S_1{-}3p\ {}^2P_1$	1402.770	.769 (12)
${}^2S_1{-}\quad {}^2P_2$	1393.755	.755 (15)
$4p\ {}^2P_2{-}5d\ {}^2D_2$	1368.573*	
${}^2P_2{-}\quad {}^2D_3$	1368.571*	
${}^2P_1{-}\quad {}^2D_2$	1365.549*	
$4p\ {}^2P_2{-}6s\ {}^2S_1$	1230.795*	
${}^2P_1{-}\quad {}^2S_1$	1228.349*	
$4s\ {}^2S_1{-}5p\ {}^2P_1$	1211.757*	
${}^2S_1{-}\quad {}^2P_2$	1210.652*	
$3p\ {}^2P_2{-}3d\ {}^2D_3$	1128.340	.340 (10)
${}^2P_2{-}\quad {}^2D_2$	1128.325	
${}^2P_1{-}\quad {}^2D_2$	1122.485	.486 (8)
$3d\ {}^2D_2{-}4f\ {}^2F_3$	1066.650	.629 (8)[1]
${}^2D_3{-}\quad {}^2F_3$	1066.636	
${}^2D_3{-}\quad {}^2F_4$	1066.614	
$4p\ {}^2P_2{-}6d\ {}^2D_{3,2}$	1047.271*	
${}^2P_1{-}\quad {}^2D_2$	1045.500*	
$4s\ {}^2S_1{-}6p\ {}^2P_1$	895.558*	
${}^2S_1{-}\quad {}^2P_2$	895.228*	
$3d\ {}^2D_2{-}5p\ {}^2P_1$	861.118	
${}^2D_2{-}\quad {}^2P_2$	860.560	
${}^2D_3{-}\quad {}^2P_2$	860.551	
$3p\ {}^2P_2{-}4s\ {}^2S_1$	818.128	.129 (8)
${}^2P_1{-}\quad {}^2S_1$	815.053	.049 (7)
$3d\ {}^2D\ {-}5f\ {}^2F$	749.939	.941 (5)
$3d\ {}^2D_2{-}6p\ {}^2P_1$	688.395	
${}^2D_2{-}\quad {}^2P_2$	688.200	
${}^2D_3{-}\quad {}^2P_2$	688.194	
$3d\ {}^2D\ {-}6f\ {}^2F$	645.764	.759 (2)
$3p\ {}^2P_2{-}4d\ {}^2D_{3,2}$	560.980	
${}^2P_1{-}\quad {}^2D_2$	559.533	
$3p\ {}^2P_2{-}5s\ {}^2S_1$	516.344	.348 (3)
${}^2P_1{-}\quad {}^2S_1$	515.118	.118 (2)
$3s\ {}^2S_1{-}4p\ {}^2P_1$	458.155	.155 (3)
${}^2S_1{-}\quad {}^2P_2$	457.815	.818 (4)
$3p\ {}^2P_2{-}5d\ {}^2D_{3,2}$	455.065	
${}^2P_1{-}\quad {}^2D_2$	454.112	
$3p\ {}^2P_2{-}6s\ {}^2S_1$	438.734	
${}^2P_1{-}\quad {}^2S_1$	437.849	
$3p\ {}^2P_2{-}6d\ {}^2D_{3,2}$	412.939	
${}^2P_1{-}\quad {}^2D_2$	412.155	
$3s\ {}^2S_1{-}5p\ {}^2P_1$	361.659	
${}^2S_1{-}\quad {}^2P_2$	361.560	
$3s\ {}^2S_1{-}6p\ {}^2P_1$	327.181	
${}^2S_1{-}\quad {}^2P_2$	327.137	

[1] Edlén and Söderqvist (1933) gave the observed value λ 1066.622.

The series limit and series formulae

The series limit, $E_0 = T + E$, where T is the absolute term value, can be derived in different ways. The method that is probably best in the present case is the application of the polarization formula to the hydrogen-like terms. The polarization energy Δ_p may be defined by $T = T_H + \Delta_p$, where T_H is the hydrogenic term value. $T_H = \dfrac{R\zeta^2}{n^2} + \Delta_r$, with $\Delta_r = \dfrac{R\alpha^2\zeta^4}{n^4}\left(\dfrac{n}{l+\frac{1}{2}} - \dfrac{3}{4}\right)$, R being the Rydberg constant for silicon, ζ the net charge of the atomic core ($\zeta = 4$), and α the Sommerfeld fine-structure constant. By taking account not only of the dipole polarizability of the atomic core but also

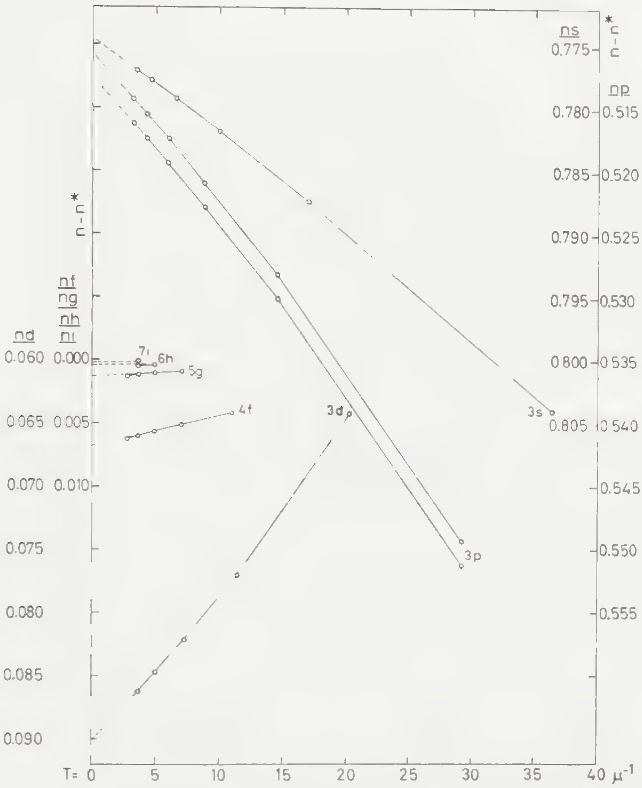

Fig. 4. The quantum defects, $n - n^*$, for the term series of Si IV. The undisturbed series *nf*, *ng*, *nh*, and *ni* are represented by dashed lines.

of the quadrupole distortion and penetration, Δ_p can be written $\Delta_p = AP(n,l)(1 + kr(n,l))$, where $P(n,l)$ and $r(n,l)$ are given by theory as rational functions of the orbital quantum numbers n and l of the valence electron. These functions may be calculated from Bockasten's (1956) tables of $\varphi(n,l)$ and $\psi(n,l)$ and the relations $P(n,l) = R\varphi(n,l)$ and $r(n,l) = \psi(n,l)/\varphi(n,l)$. A and k are treated as parameters to be determined from observed term values.

In order to determine the correct value of E_0 it is convenient to start with an approximate value E_0' and the corresponding values T', and derive the correction ΔT. By means of the relation $(T' + \Delta T) - T_H = AP(n,l)(1 + kr(n,l))$ the correction ΔT and the two parameters A and k can be determined from three observed term values. The terms used must be sufficiently hydrogen-like to make the formula applicable. At the same time the influence of the Stark effect should be as small as possible, and Δ_p should not be too small. With regard to these requirements the terms $4f\,^2F$, $5f\,^2F$, and $5g\,^2G$ were chosen. From the three equations obtained one can first eliminate ΔT and then determine A and k. With the values $R = 109737.31 - 60.20/M = 109735.17$ cm^{-1} (where $M = 28.09$ is the atomic weight of silicon), $R\alpha^2 = 5.843$ cm^{-1}, and $\zeta = 4$ the calculation gives

$$A = 38.107, \quad k = 22.162, \quad E_0 = 364093.1 \text{ cm}^{-1}.$$

Table 5. Ritz formulae for the term series of Si IV.

$T = 1\,755\,762.72/(n-\delta)^2,\ t = (n-\delta)^{-2}.$

The residuals $T_{\text{obs}} - T$ (formula) are given in cm^{-1}.

$ns\ {}^2S_{\frac{1}{2}}$: (I) $\delta = 0.774\,582\,4 + 0.122\,915\,7\,t + 0.092\,016\,t^2$

	T_{obs}–(I)
$3s$	(0)
$4s$	(0)
$5s$	(0)
$6s$	+ 0.01
$7s$	– 0.07
$8s$	+ 0.12

$$np\ {}^2P_{\frac{1}{2}} \begin{cases} \text{(I)} & \delta = 0.512\,909\,0 + 0.184\,546\,0\,t + 0.272\,227\,t^2 \\ \text{(II)} & \delta = 0.512\,774\,6 + 0.189\,661\,1\,t + 0.213\,967\,t^2 + 0.194\,39\,t^3 \\ \text{(III)} & \delta = 0.512\,801\,5 + 0.187\,995\,3\,t + 0.246\,281\,t^2 \end{cases}$$

	T_{obs}–(I)	T_{obs}–(II)	T_{obs}–(III)
$3p$	(0)	(0)	+ 57.6
$4p$	(0)	(0)	(0)
$5p$	(0)	(0)	(0)
$6p$	– 0.46	(0)	(0)
$7p$	– 0.48	+ 0.07	+ 0.04
$8p$	– 0.42	+ 0.09	+ 0.03

$$np\ {}^2P_{\frac{3}{2}} \begin{cases} \text{(I)} & \delta = 0.510\,978\,3 + 0.184\,717\,6\,t + 0.273\,819\,t^2 \\ \text{(II)} & \delta = 0.510\,823\,7 + 0.190\,606\,5\,t + 0.206\,667\,t^2 + 0.224\,35\,t^3 \\ \text{(III)} & \delta = 0.510\,854\,7 + 0.188\,687\,5\,t + 0.243\,927\,t^2 \end{cases}$$

	T_{obs}–(I)	T_{obs}–(II)	T_{obs}–(III)
$3p$	(0)	(0)	+ 66.6
$4p$	(0)	(0)	(0)
$5p$	(0)	(0)	(0)
$6p$	– 0.53	(0)	(0)
$7p$	– 0.53	+ 0.10	+ 0.06
$8p$	– 0.32	+ 0.27	+ 0.20

$$nd\ {}^2D \begin{cases} \text{(I)} & \delta = 0.089\,898\,9 - 0.170\,012\,1\,t - 0.439\,418\,t^2 \\ \text{(II)} & \delta = 0.090\,158\,1 - 0.182\,503\,7\,t - 0.254\,535\,t^2 - 0.831\,49\,t^3 \\ \text{(III)} & \delta = 0.090\,094\,3 - 0.177\,743\,2\,t - 0.366\,706\,t^2 \end{cases}$$

	T_{obs}–(I)	T_{obs}–(II)	T_{obs}–(III)
$3d$	(0)	(0)	– 40.0
$4d$	(0)	(0)	(0)
$5d$	(0)	(0)	(0)
$6d$	+ 0.57	(0)	(0)
$7d$	+ 0.66	– 0.10	– 0.04

Table 6. Comparison between calculated and observed values of the hydrogen-like terms of Si IV.

Δ_p (calc) $= 38.107\ P(n, l)\ [1 + 22.162\ r(n, l)]$						T, calc cm^{-1}
Term	Δ_r cm^{-1}	T_H cm^{-1}	Δ_p (calc) cm^{-1}	Δ_p (obs) cm^{-1}	Δ_p (obs) $-$ Δ_p (calc)	
$4f\ ^2F$	2.30	109 737.47	227.39	227.39	(0)	109 964.86
$5f\ ^2F$	1.62	70 232.13	141.93	141.93	(0)	70 374.06
$6f\ ^2F$	1.11	48 772.30	90.36	90.48	0.12	48 862.66
$7f\ ^2F$	0.78	35 832.67	60.07	60.34	0.27	35 892.74
$8f\ ^2F$	0.56	27 434.35	41.64	42.15	0.51	27 475.99
$5g\ ^2G$	0.87	70 231.38	23.75	23.75	(0)	70 255.13
$6g\ ^2G$	0.67	48 771.86	15.76	15.91	0.15	48 787.62
$7g\ ^2G$	0.50	35 832.39	10.70	11.02	0.32	35 843.09
$8g\ ^2G$	0.38	27 434.17	7.51	8.19	0.68	27 441.68
$6h\ ^2H$	0.39	48 771.58	4.54	4.11	-0.43	48 776.12
$7h\ ^2H$	0.33	35 832.22	3.20	3.71	0.51	35 835.42
$8h\ ^2H$	0.26	27 434.05	2.28			27 436.33
$7i\ ^2I$	0.20	35 832.09	1.19	0.20	-0.99	35 833.28
$8i\ ^2I$	0.18	27 433.97	0.87			27 434.84
$8k\ ^2K$	0.12	27 433.91	0.37			27 434.28

The error in E_0 is believed not to exceed 0.6 cm^{-1}. E_0 is equal to the absolute term value T for $3s\,^2S$. The T values are given in column 4 of Table 3, and the values of n^*, calculated according to the formula $n^* = \sqrt{\frac{R\,\zeta^2}{T}}$, are given in column 5. It appears that Δn^* is very nearly constant for $np\ ^2P_{2,1}$. The quantum defects $\delta = n - n^*$, are plotted against T in Fig. 4.

The term series ns, np and nd can be represented by extended Ritz formulae (cf. Edlén and Risberg, 1956). Table 5 shows how the observations fit the formulae determined for the different series. It appears that the series ns can be well represented by a three-constant formula. For the series np and nd it is necessary either to omit the lowest term or to use a formula containing four constants. The term value for $8d\ ^2D$ has been extrapolated by means of formula III for the d series.

With the parameters A and k, calculated as above, the polarization formula gives the possibility of calculating unaffected term values for all hydrogen-like series with $l \geqslant 3$. Calculated and observed values of Δ_p are compared in Table 6. It is seen that the difference $\Delta_p(\text{obs}) - \Delta_p(\text{calc})$ shows a deviation increasing with n in each series. Between levels with the same n there is also a tendency toward larger differences as the quantum number l increases. These deviations may be explained qualitatively in terms of the Stark effect (cf. Bockasten, 1956) if the field strength in the spark is assumed to be of the order of 12 kV/cm. The calculated, unperturbed term-values are shown in the last column of Table 6.

Description of Plate I

In Plate I are shown spectrograms of a sliding vacuum-spark with silicon electrodes and an insulating disk of quartz. The disk was divided into two parts for the spectrograms *a* and *b*. A stigmatic 21-foot concave-grating spectrograph was used in the first order for the spectrograms *a* and *b* (4.83 Å/mm), and in the second order for *c*, *d*, *e*, and *f* (2.36 Å/mm). The shapes and intensities of the Si III and Si IV lines depend on the conditions in the spark, as is shown in *c*, *d*, *e*, and *f*. The spectrograms also give a picture of the Stark effect for the hydrogen-like transitions 5–6 and 6–7.

Spark data and time of exposure for each spectrogram were as follows:

Spectrogram	Condenser μF	External spark gap mm	Induction coil, number of turns*	Exposure time, minutes
a	0.30	6	20	60
b	0.30	8	15	60
c	0.30	4	29	5
d	0.30	2	29	15
e	0.30	4	29	15
f	0.30	6	15	15

* Each turn gives an inductance of 2 μ H.

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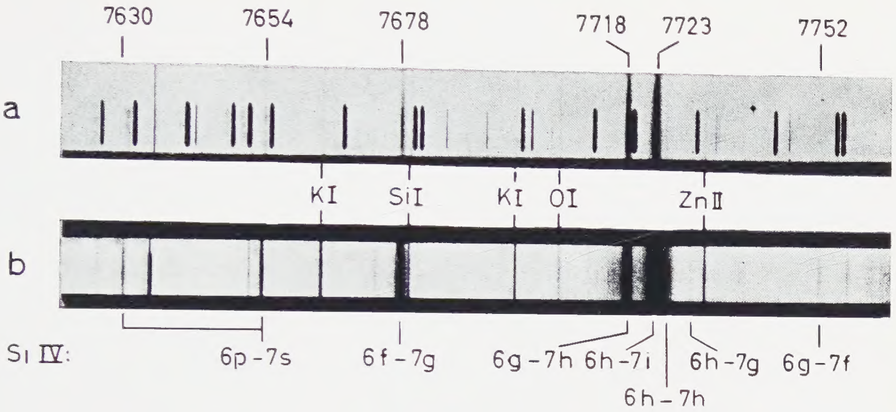
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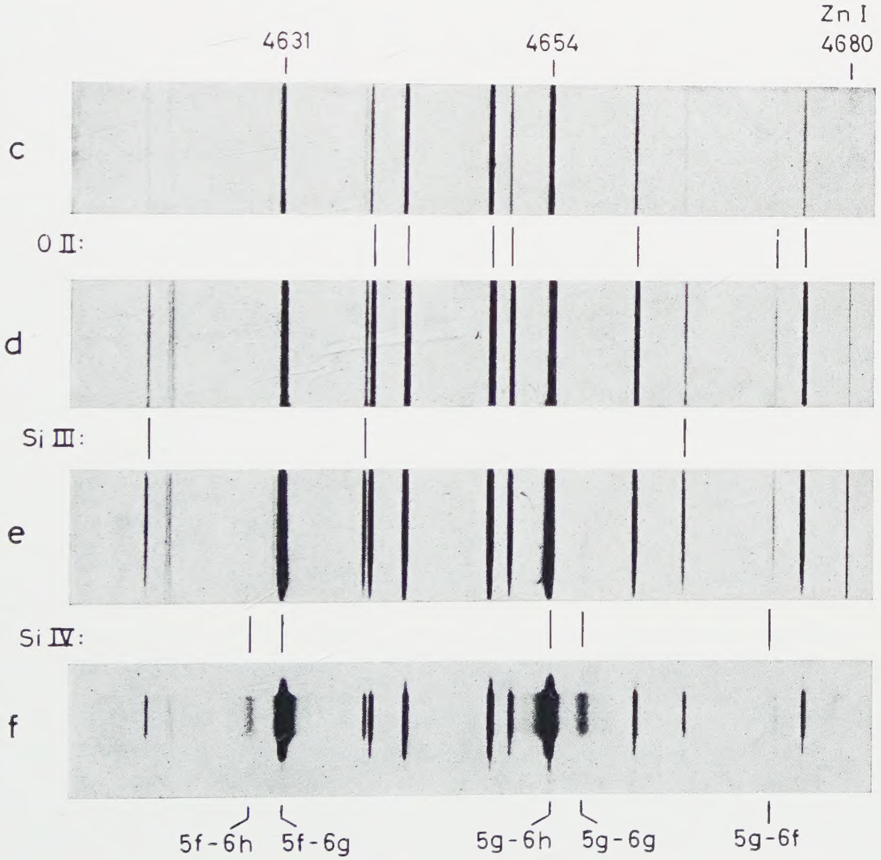
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